

ORIGINAL



W7

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :

G21B 1/00

A1

(11) International Publication Number:

WO 94/14163

(43) International Publication Date:

23 June 1994 (23.06.94)

(21) International Application Number:

PCT/US93/11754

(22) International Filing Date:

3 December 1993 (03.12.93)

(81) Designated States: AU, CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

(30) Priority Data:

07/958,483

10 December 1992 (10.12.92)

US

Published

With international search report.

(71) Applicant: ELECTRIC POWER RESEARCH INSTITUTE, INC. [US/US]; 3412 Hillview Avenue, Palo Alto, CA 94303 (US).

(72) Inventors: MCKUBRE, Michael, C., Jr.; 112 Durham Street, Menlo Park, CA 94025 (US). ROCHA-FILHO, Romeu, C.; Rue Estados Unidos, 949, 13560-São Carlos, SP (BR). SMEDLEY, Stuart, L.; 364 O'Connor Street, Menlo Park, CA 94025 (US). FANZELLA, Francis, L.; 935 Buckland Avenue, San Carlos, CA 94070 (US). CROUCH-BAKER, Steven, 3120 Louis Road, Palo Alto, CA 94303 (US). SANTUCCI, Joseph; 321 Quinns Hill, Los Altos, CA 94022 (US).

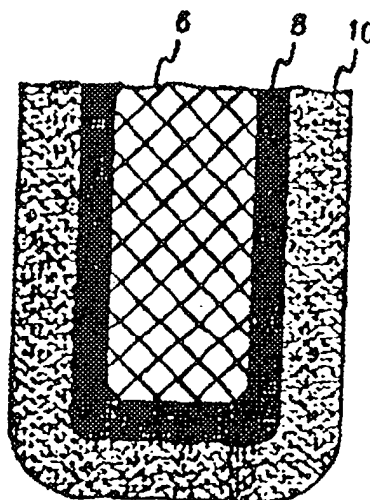
(74) Agents: GALLIANI, William, S. et al.; Flehr, Hobbach, Test, Albritton &amp; Herbert, 4 Embarcadero Center, Suite 3400, San Francisco, CA 94111-4187 (US).

COPY

(54) Title: METHODS FOR FORMING FILMS ON CATHODES

(57) Abstract

A method for forming a film (10) on the surface of a cathode (7) to facilitate the loading of a hydrogen isotope into the cathode (7). The cathode (7) and an anode (9) are immersed in an electrolyte (5) containing a hydrogen isotope and conducting ions, and the electrodes are connected to a current source (11). The conducting ions may be formed by inclusion of LiOH or LiOD or LiOI in the electrolyte (5). The addition of other elemental species or compounds to the electrolyte (5) further promotes the film (10) formation and enhances the loading of the hydrogen isotope into the cathode (7).



7

## METHODS FOR FORMING FILMS ON CATHODES

### Background of the Invention

#### 1. *Field of the Invention*

This invention relates to methods for forming films on cathodes, particularly films for facilitating electrochemical charging of metals and alloys with isotopes of hydrogen (H).

#### 2. *Description of Background Art*

The formation of compounds involving hydrogen isotopes in combination with certain metals and alloys is important because these compounds may be used for the storage of hydrogen isotopes and as battery electrodes. Such storage of hydrogen is useful any time one wishes to subsequently oxidize the hydrogen to produce energy, e.g., for transportation or in a fuel cell. The application of this invention to battery electrodes can be for vehicle propulsion batteries and alternatives to nickel cadmium batteries.

The electrochemical charging of metal cathodes with hydrogen is a known method for producing these so-called "hydrogen storage alloys". In this connection, the formation of films

*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LJ	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

on the metal cathodes can be important, as loading may be affected by the film. In addition, the formation of films on palladium cathodes can be important because excess power evolution has been observed during the electrochemical loading of the hydrogen isotope deuterium into palladium cathodes, and this loading may be affected by the film. Such excess power evolution has become known collectively under the generic title of "cold fusion". The precise origin of the evolved energy is presently open to some debate, and the conditions under which it is reproducibly obtained have not hitherto been defined.

#### Disclosure of Invention

A method of forming a film (10) on the surface of a cathode (7) to facilitate the loading of an isotope of hydrogen into the cathode (7). The cathode (7) is immersed with an anode (9) in an electrolyte (5) containing an isotope of hydrogen and conducting ions, and both electrodes (7), (9) are connected to a current source (11) for promoting electrolysis and providing energy. Conducting ions may be formed by the inclusion of LiOH or LiOD or LiOT in the electrolyte. The addition of further elemental species or compounds to the electrolyte promotes the formation of the film (10), and this film (10) enhances the charging of the cathode (7) with the isotope of hydrogen from the electrolyte (5). The preferred embodiments described below are concerned with the specific example of the charging of a palladium cathode (7) with deuterium (D).

#### Brief Description of the Drawings

FIG. 1 is a partly schematic diagram of an electrolysis system 1 generic to the specific examples of apparatus for carrying out the steps of the present invention;

FIG. 2 is a perspective diagram of an example of the electrolysis system 1 of FIG. 1, showing two gas permeable anodes 51 and thin film cathode 52;

FIG. 3 is a partly schematic diagram of an example of the electrolysis system 1 of FIG. 1, including metal cup 53;

FIG. 4 is a front cross-sectional view of electrolysis cell 22 described in Example 1 herein;

FIG. 5a is a front view of electrolysis cell 40 described in Example 2 herein;

FIG. 5b is a front cross-sectional view of electrolysis cell 40 described in Example 2 herein;

FIG. 6 is a front cross-sectional view of electrolysis cell 67 described in Example 3 herein; and

FIG. 7 is a partial cross-sectional view of a cathode 7 which may be used in all examples illustrated herein.

#### Description of the Preferred Embodiments

FIG. 1 shows a schematic diagram of electrolysis system 1 suitable for practicing the method of the present invention, for loading deuterium into a palladium cathode 7. Electrolysis system 1 includes container 3 filled with electrolyte 5. The system 1 may be enclosed in a pressurized or sealed enclosure 2, which may also serve as a heat exchanger or may comprise various heat exchange devices, well known in the art, for extracting and transferring heat from the system. The electrolysis system 1 also includes two electrodes 7,9 at least partially immersed in electrolyte 5. A current source 11 is connected between electrodes 7,9 to generate a flow of ions within electrolyte 5 between the two electrodes 7,9. A voltage measuring device 4 indicates the potential difference

between the electrodes 7,9. Cathode 7 preferably is constructed of a metallic bulk region or rod 6 having an outer layer of palladium, and anode 9 is constructed of platinum, palladium, or some stable non-elemental metallic conductor material. Although palladium is the preferred surface material for use in the cathode 7, other materials such as palladium alloys are suitable substitutes. The bulk region may be constructed of metal having a low deuterium permeability, such as copper.

10 As shown in Fig. 7, the surface of cathode 7 preferably comprises a metal 8 having a crystal structure such that roughly polyhedral spaces are enclosed by the metal atoms in the crystal lattice. For example, palladium has a face-centered cubic crystal structure with roughly octahedral  
15 interior spaces. Deuterium atoms can occupy these sites. The palladium structure 8 thus acts as a storage medium for deuterium. In addition, this association of deuterium within the palladium host material causes a phenomenon which results in the release of heat. The purpose of the  
20 electrolysis system 1 is to cause deuterium to be drawn to the negatively biased cathode 7 in order to load the metal 8 with deuterium. After the deuterium is loaded into the metal 8, excess heat is generated when the deuterium interacts with other elemental species in the vicinity of  
25 cathode 7. The interaction may occur between deuterium atoms or deuterium and H, D; Li, B or Pd.

FIG. 1 shows a system 1 having a single electrolysis cell 12 comprising anode 9 and cathode 7. Alternatively, a plurality of such cells 12 may be connected together.

### 30 Palladium (Pd) 7

The palladium cathode may be fabricated, either in the form of a Pd rod electrode 7, or in the form of a Pd layer 8 electrodeposited onto a Cu rod 6. The bulk Pd should be of high purity, and typically it is annealed in a vacuum

furnace at 800°C for three hours and then allowed to cool in 1 atm. of D<sub>2</sub> gas or argon. The purpose of the heat treatment is to volatilize impurities from the layer 8, and to anneal out crystal imperfections.

- 5 Cooling the metal in a D<sub>2</sub> atmosphere facilitates partial loading of the metal 8 with deuterium gas, while avoiding the mechanical stress induced in crossing the two-phase miscibility gap. It is important at all stages of treatment to minimize stresses that may lead to cracking of the palladium deuteride (PdD<sub>x</sub>), since high loading cannot be  
10 attained or maintained by electrochemical means if cracks propagate to the surface of the metal 8.

High temperature gas loading also helps prevent the ingress of unwanted O<sub>2</sub> and H<sub>2</sub>O when, for short times, cathode 7 is  
15 exposed to the atmosphere. Oxidation of the surface of cathode 7 by O<sub>2</sub> or H<sub>2</sub>O reduces the ability of Pd to absorb D. In the case that the Pd is required to absorb only D, hydrogen produced by corrosion of Pd in H<sub>2</sub>O may absorb into sites that D otherwise could occupy.

- 20 Once cooled, the Pd surface is etched in deuterated aqua regia and then rinsed in D<sub>2</sub>O. This process removes any oxide film from the surface of the metal 8 and aids loading by enhancing the kinetics of D adsorption-desorption.

#### Electrolyte 5

- 25 The electrolyte 5 of choice is LiOD. LiOD is simple to prepare, and yields products of electrolysis which are nearly 100% D, and O<sub>2</sub>. In order to minimize the amount of unwanted H<sub>2</sub>O, O<sub>2</sub> and CO<sub>2</sub> in electrolyte 5, solution 5 is formed by reacting pure Li metal or Li<sub>2</sub>O with D<sub>2</sub>O of high  
30 isotopic purity in an inert gas environment.

## Electrochemical Cell 12 Specifications

In electrochemical cells 12 designed for loading deuterium gas into cathode 7, it is important to provide a uniform current over as much of the surface of cathode 7 as possible. The deuterium ions which dissolve into the metal 7 are in a state of dynamic equilibrium with the gas phase of deuterium, and the transfer of surface adsorbed molecules to the absorbed state is rapid and reversible. As a consequence, metal 7 will charge with the gas as long as the inward flux of deuterium ions is greater than the outward flux of deuterium gas. In non-uniform current fields, cathode 7 may load unevenly, allowing the deuterium entering from the areas of high current density, and presumably high loading, to leak away to the areas of low current and presumably low loading. Also, in order to minimally interfere with the current distribution, potential sensing and current contacts 15,43 must be placed at the end of cathode 7.

The requirement for a uniform current density can be met if:  
1) all points on the cathode 7 surface have the same potential; and 2) all points on anode 9 are at the same potential. A symmetrical electrode 7,9 arrangement, such as a rod cathode 7 and a coaxial anode 9 of cylindrical geometry (as in FIGS. 4-6), meets these constraints. Another approach that meets these conditions over most of cathode 7 is shown in FIG. 2, where a thin-film type of cathode 52 is sandwiched between two gas permeable anodes 51. A further consequence of the above requirements is that cathode 52 must be fully immersed in electrolyte 50 in order to prevent gas leakage from cathode 52.

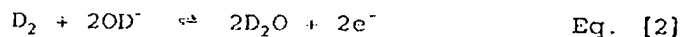
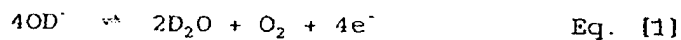
As stated above, the extent to which cathode 7 can be loaded with  $D_2$  depends on the surface conditions. Materials which deposit on cathode 7 as a result of prolonged electrolysis can severely affect the rate of ingress of gas into the metal 7, and, consequently, the degree of loading. Because



of this, it is necessary to be careful about the choice of anode 9 and cell container 3 materials. Quartz glass and polytetrafluoroethylene (PTFE) are examples of suitable container 3 materials. For the same reason, anode 9 metals other than Pt or Pd should be avoided; stable electronically conductive non-elemental metallic anodes 9 are suitable.

#### Method of Cell 12 Construction

All electrochemical cells 12 contain an anode 9 and a cathode 7. The predominant cathode 7 reaction of the present invention is the reduction of  $D_2O$ . The anode 9 reaction is a mixture of two reactions:



The relative contributions of these to the anode 9 current are determined by the kinetics of each reaction. If the predominant anode 9 reaction is described by Eq. [1], then the minimum cell voltage measured by the voltage meter 4 will be 1.27 volts at room temperature, after deuterium loading has occurred. When the minimum cell 12 voltage 4 is applied, there is no net electrochemical current in the cell. Under operating conditions, increased values of the electrochemical current are required. As current from the source 11 is increased, the cell 12 voltage 4 rises rapidly due partly to the overvoltage required for oxygen evolution described in Eq. [1]. On the other hand, if the reaction of Eq. [2] predominates, then the minimum cell 12 voltage 4 is 0 volts, after deuterium loading has occurred. At the minimum cell 12 voltage 4, there is no net electrochemical current in the cell. Under operating conditions, increased values of the electrochemical current are required, and the cell 12 voltage 4 will not rise as rapidly with increasing current 11, because of the very fast kinetics of this reaction.

There are at least two advantages attributable to the Eq. [2] reaction. The first advantage is that the electrolysis system 1 can be operated under reducing conditions (i.e. absence of free oxygen). In cells 12 that produce oxygen, there is always the possibility that the cathode 7 surface will react with the oxygen to produce an oxide layer which acts as a barrier for deuterium transport across the electrolyte 5/metal 7 interface. This is not conducive to the achievement of a high D/Pd atomic ratio. Generally speaking, a high D/Pd ratio is desirable.

The second advantage to the reaction of Eq. [2] is that the ratio of excess power to input power can be maximized. Experimental evidence shows that excess heat increases with increasing current density, and with this Eq. [2] reaction, high current densities can be achieved with a relatively low input power (i.e., low cell 12 voltage 4). For commercial applications, this provides a cost benefit.

The technique disclosed herein embodies several features which promote the Eq. [2] reaction at anode 9. The Eq. [2] reaction is kinetically very fast, and even at low current densities is diffusion controlled; whereas the Eq. [1] reaction cannot be diffusion controlled for an electrolyte 5 that contains mostly  $D_2O$ . In order to promote the reaction of Eq. [2], the supply of  $D_2$  to the anode 9 surface must be significantly enhanced. A method of achieving this enhancement is by increasing the concentration of  $D_2$  in electrolyte 5. The  $D_2$  concentration in electrolyte 5 can be increased by exposing electrolyte 5 to high pressure  $D_2$ . Other ways of increasing the supply of  $D_2$  to the anode 9 surface are by utilization of gas permeable anodes 51 (FIG. 2), or by using a very small anode 9 to cathode 7 spacing. The gas permeable electrode 51 shown in FIG. 2 is a porous structure that significantly increases the three phase contact area between the deuterium, the electrolyte 5, and the metal phase of anode 51.

Another way to increase the supply of deuterium to the anode 9/electrolyte 5 interface is to contain electrolyte 5 in a metal cup 53, that is highly permeable to deuterium, and to suspend cup 53 in high pressure deuterium gas 54, as shown in FIG. 3. Metallic cup 53 serves as an anode through which current introduced by current source 45 can cause electrolyte 47 ions and  $D_2O$  to interact with cathode 52. The high pressure deuterium gas 54 surrounding cup 53 maintains a high concentration of deuterium at the anode 53/electrolyte 47 interface and promotes the Eq. [2] reaction described above.

Apart from the ability to operate under pressure, enclosing electrolysis system 1 in a sealed enclosure 2, 49 has several other advantages. The electrolyte 5,47 is retained, which avoids the need for replenishment of  $D_2O$ ; and the system 1 is sealed from substances (such as  $H_2O$ ) that are deleterious to high deuterium loadings and excess heat production.

#### Electrochemical Treatment

For optimum loading, cathode 7 should be pre-charged at a moderate current density (between 10 and 100  $mA/cm^2$ ) for a time corresponding to three or more diffusion periods. A diffusion period is represented approximately by  $x^2/D$ , where  $x$  is the thickness of the metal layer 8, and  $D$  is the average chemical diffusion coefficient of deuterium in the metal 8. For cylindrical cathodes 7 of radius between 3 mm and 5 mm, currents of between 10  $mA/cm^2$  and 100  $mA/cm^2$  are typically used for a time of between 3 days and 10 days. If the cathode 7 preconditioning and electrolyte 5 conditions are as described above, the average atomic ratio (D/Pd) generally achieved in the steady state will be between 0.8 and 0.95. A high loading ratio is important for the initiation of heat generation. Ratios of at least 0.8 (preferably at least 0.9) are required. A D/Pd ratio of unity or higher is even better. The loading can be

determined by measuring the resistance of cathode 7, as discussed below.

In addition to facilitating loading, maintaining a moderate current density for a further period of time facilitates the formation of a film 10 on the solution side of the cathode 7/electrolyte 5 interface. Aluminum (Al) introduced as an additive species to electrolyte 5 has been observed to further promote this film 10 formation. Alternatively, Si and B are satisfactory additive species to electrolyte 5. In addition, other elements believed to promote film 10 formation include Ba, Ca, Cu, Fe, Li, Mg, Ni, Sc, Ti, V, Y, and Zr. The film 10 is believed to be gelatinous in form, and therefore of an ill-defined thickness, during electrolysis. After completion of the process, only a dehydrated version of the film 10 can be observed and tested. This dehydrated version of the film 10 can have a thickness of approximately 1 micron. The composition of the film 10 derives from the additive species as well as elements from components involved in the process. The composition of the film 10 in its gelatinous form is impossible to determine, but the composition of the dehydrated version of the film 10 has been determined to be approximately 10 wt% Pt, 2 wt% Si, 1 wt% Al, 1 wt% Na, and unknown percentages of C and O, in a specific embodiment described in Example 3.

Time must be provided for Li and the additive species to diffuse and electromigrate into the Pd solid 7 from electrolyte 5; and for minority element segregation to occur by diffusion within the beta-phase  $PdD_x$  and by electromigration within the metal phase.

Film 10 formation (see Fig. 7) through the addition of elemental species to electrolyte 5 results in improved absorption of deuterium into the palladium 7. This film 10 is believed to improve absorption by several mechanisms. First, the film 10 serves as a deuterium ion ( $D^+$ ) conductor

to facilitate the transport of desirable species ( $D'$ ) to the Pd layer 8 while selecting against the transport of electrolyte 5 impurity cations that may deposit onto the surface of cathode 7. Such deposited species may prevent D absorption by acting as an impermeable layer or by catalyzing the alternate process of recombination ( $D_{ads} + D_{ads} \leftrightarrow D_2, gas$ ). Second, film 10 serves to hinder recombination by blocking molecular adsorption sites and preventing atomic and molecular diffusion on the surface of cathode 7. Third, film 10 serves to prevent the nucleation of  $D_2$  gas bubbles, thereby increasing the effective pressure of deuterium and the limit of loading ( $D/Pd$ ). Finally, to the extent film 10 forms over cracks and other Pd surface imperfections, deloading at these sites is reduced or prevented.

15 The existence of a surface film 10, its character, and its role in facilitating loading can be determined from the results of electrochemical impedance measurements of the cathode 7/electrolyte 5 interface.

The onset of excess heat production is initiated by increasing the current density. This has the effect of increasing the loading until the average loading,  $D/Pd$ , increases to a level sufficient to generate excess heat. For Pd cathodes 7 of diameter between 3 and 8 mm, this has been observed at loading ratios between 0.95 and 1.0, for current densities on the order of 300 mA/cm<sup>2</sup>.

A cathode 7 that is adequately loaded for a sufficient period of time and subjected to a sufficient interfacial current density will yield excess heat. High currents are desirable for three reasons: to attain high loading, to attain D fluxes in the metal phase, and to permit a film 10 to form appropriately at the cathode 7 and electrolyte 5 interface.

In many cases, it is not possible to achieve or to maintain high loading levels. Significant causes of this deficiency

are: the presence on the Pd surface 7 of hydrogen (deuterium) recombination catalysts (e.g., Pt); the existence of cracks in the metal 8; excessive temperatures; and fluctuating currents. One role of the surface film 10 is to prevent the migration to the surface 8 of species introduced with electrolyte 5, from anode 9, or from container 3 that, when deposited on cathode 7, will catalyze  $D_2$  recombination.

If adequate loading is not achieved or has not been maintained, it sometimes is possible to remove surface 8 active agents that are deleterious to loading and to restructure the Pd surface film 10 to facilitate reloading. This can be accomplished by holding Pd cathode 7 anodic at a sufficient current density and for a sufficient time to raise the potential of the Pd to the point where oxygen evolution just begins to dominate deuterium oxidation. It is not desirable to evolve oxygen on Pd cathode 7 at any significant rate, as the surface oxide that forms resists reduction and is a barrier to the entry of deuterium on subsequent cathodization. Following this anodic treatment, the surface 8 should be held cathodic at current densities of at least several  $mA/cm^2$  for a day or more to reform the surface film 10. Then the generation of excess heat can be obtained by increasing the current density.

Having now described general features and characteristics of the invention, detailed below are three examples of structures in which it may be practiced.

#### Example 1

##### Cell 22

Referring now to FIG. 4, a medium pressure cell 22 is shown. A vessel 21 is constructed of copper and has a cylindrical sleeve shape with an internal surface of platinum, which acts as the anode 19. Positioned along the central axis of

vessel 21 is palladium cathode 31. Cathode 31 is cylindrical in shape and contains voltage connectors 15 on each end. Separating cathode 31 and anode 19 is electrolyte 27 consisting of LiOD in D<sub>2</sub>O. A temperature sensor 32  
5 penetrates vessel 21 to contact cathode 31.

In order to avoid electrolyte 27 contamination during operation, the electrolyte 27 is exposed only to the materials palladium, platinum and polytetrafluoroethylene (PTFE). The inner surfaces of cell 22, as well as the  
10 surfaces of the copper and brass fittings external to the portions of cell 22 exposed to the electrolyte 27, are coated with a 25 micron nickel (Ni) film and a 5 micron film of Pt deposited using an electrolysis plating method. All metal and PTFE cell 22 surfaces are solvent cleaned and  
15 rinsed. The Pt coated surfaces are further washed with aqua regia and rinsed with D<sub>2</sub>O.

#### *Cathode 31*

Palladium cathode 31 is a 7mm dia., 4 cm long Pd rod, machined from a twice-melted pure Pd source. A 2mm threaded  
20 hole 30 is machined in the center of the side of cathode 31 to accept temperature sensor 32. Once machined, cathode 31 is vacuum annealed at 800°C for two to three hours and cooled in one atmosphere of D<sub>2</sub>. Cathode 31 is next dipped in aqua regia for 20 seconds and rinsed with D<sub>2</sub>O immediately  
25 before cell 22 assembly.

#### *Electrolyte 27 Preparation*

The 0.1M LiOD electrolyte 27 is prepared by adding 0.035g Li metal (Aesar 99.9% used as received) to 50 ml D<sub>2</sub>O (Aldrich 99.9 atom % D, as received). This preparation is carried  
30 out under a nitrogen atmosphere, preferably immediately prior to use.

## Cell 22 Assembly

Cell 22 is assembled with minimum exposure to air or  $H_2O$  by threading the ends of cathode 31 into one of two end-pieces 25. This end-piece 25 is then sealed into the body of vessel 21 using a PTFE sealing ferrule and a Cu nut 24. An opposing end-piece 25 is similarly threaded onto cathode 31 in vessel 21 and sealed in place. A 2mm Pt coated Cu tube 29 containing temperature sensor 32 is passed through the side wall of vessel 21 and sealed into threaded hole 30 in cathode 31.

Exposed areas of end-pieces 25 and temperature sensor tube 29 are coated with epoxy and PTFE to electrically insulate them from electrolyte 27. Electrical connections are made to voltage connections 15 and current connections 23 to measure the Pd resistance and introduce the electrolyzing current. A 1/8" outside diameter Cu gas inlet 17, extending to an external manifold, is sealed to a threaded hole on the wall of vessel 21 above the level of electrolyte 27. Vessel 21 is maintained in a constant temperature water bath at 7°C and pressurized to 300 psig with  $D_2$  via inlet 17.

Measurements of cell 22 voltage and Pd cathode 31 temperature are made and recorded by computer every two minutes. Palladium resistance measurements are made manually by passing up to 10A of alternating current between cathode current connections 23, and then measuring the voltage drop along cathode 31 between voltage connections 15. An anode connection 16 is attached to the vessel 21. The cathode current connections 23 supply current to the system while the voltage connections 15, which have no current running through them, measure the potential difference in the system. As one skilled in the art will recognize, measurement of the potential difference by use of the cathode current connections 23 would be incorrect due to the voltage contribution of the resistance in the cathode current connections 23. Pressure is read on a mechanical



pressure gauge on the external manifold and recorded manually. As the  $I_2$  diffuses into the Pd cathode 31, it is compensated by adding  $D_2$  to maintain a constant cell 22 pressure.

- 5 The foregoing apparatus is useful for performing a calorimetry experiment, in which one seeks to compare the known and measured sources of input energy or power to the system with the observed output energy or power. The difference between the output energy and input energy is  
10 defined as the "excess heat".

Using the procedure and apparatus above, a calorimetry experiment was performed over a duration of 700 hours. Excess heat was first observed after 300 hours of electrolysis and was observed in bursts on six separate  
15 occasions. The maximum excess power observed was 1.75 watts (W) (52% in excess of the input power); the total excess of energy was 0.072 Mega-Joules (MJ) or 0.33 MJ/mole of Pd.

#### Example 2

##### Cell 40

- 20 Referring now to FIGS. 5a and 5b, a medium pressure cell 40 is shown. The containment vessel 36 is constructed of Ni and has a cylindrical sleeve shape with an internal surface of Pt, which acts as the anode 41. Positioned along the central axis of vessel 36 is palladium cathode 39. Cathode  
25 39 is cylindrical in shape and contains cathode current connectors 44 and voltage connectors 43 on opposing ends. An anode connection 47 is attached to the outside of the vessel 36. Separating the cathode 39 and anode 41 is the electrolyte 38, consisting of LiOD in  $D_2O$ . A reference  
30 electrode 42 penetrates vessel 36 to contact electrolyte 38.

In order to avoid electrolyte 38 contamination during operation, the electrolyte 38 is exposed only to the

materials palladium, platinum, and polytetrafluoroethylene (PTFE). The inner surface of the Ni vessel 36, as well as the surfaces of the Ni fittings exposed to the electrolyte 38, are coated with a 25 micron Ni film via an electroless plating method and then with a 5 micron film of Pt via an electroplating method. This Pt coating serves as anode 41. All metal and PTFE cell surfaces are solvent cleaned and rinsed. The Pt coated surfaces are further washed with aqua regia and rinsed with D<sub>2</sub>O.

#### 10 Cathode 39

The Pd cathode 39 is a 3mm dia., 5 cm long Pd rod (4.5 mm exposed to electrolyte 38), machined from a 1/8" pure Pd wire. Cathode 39 is threaded 2.5mm on each end. Cathode 39 is then solvent cleaned, vacuum annealed at 800°C for two to three hours, slowly cooled in one atmosphere of D<sub>2</sub>, and maintained in the D<sub>2</sub> until cell 40 is ready for assembly.

#### *Electrolyte 38 Preparation*

The 1.0 M LiOD electrolyte 38 is manufactured by adding 0.175g Li metal to 25 ml D<sub>2</sub>O. This procedure is carried out under a nitrogen atmosphere, and electrolyte 38 is prepared immediately prior to use. A Ni cathode 39 of shape and size identical to palladium cathode 39 is temporarily assembled into vessel 36 with 20 ml of electrolyte 38. The Ni cathode 39 is held at 0.5 mA cathodic with respect to the cell wall anode 41 for three hours to help remove impurities from electrolyte 38. This pre-electrolysis is carried out under a 40 psig pressure of N<sub>2</sub> before the Ni cathode 39 is removed and discarded.

#### *Cell 40 Assembly*

An external 180 ohm steel sheathed heater (.04" diameter, 72" long) is wound in a groove 37 machined around the outside of vessel 36. Cell 40 is assembled immediately

after pre-electrolysis with minimum exposure to air or  $H_2O$ . Cathode 39 is threaded into one coated Ni end-piece 46 and inserted into vessel 36. The other end-piece 46 is then threaded onto cathode 39 in vessel 36 as above. A 3mm Ni electrode 42 coated with Pt (to be used as a pseudo-reference electrode) is sealed into the threaded hole 34 in the middle of vessel 36. A 1/8" outside diameter external Ni tube 48, extending out of vessel 36, is sealed to the pressure inlet 35, above the level of electrolyte 38. The vessel 36 is pressurized to 1000 psig with  $D_2$  via tube 48.

Cell 40 is allowed to operate for two hours to ascertain the integrity of cell 40. Cathode 39 is held at 20 mA cathodic for approximately one hour. The current is increased in 10mA steps to 50 mA over a two hour period. As the  $D_2$  diffuses into the cathode 39, it is compensated by adding  $D_2$  via tube 48 to maintain a constant cell 40 pressure.

Using this procedure and apparatus, a calorimetry experiment was performed with a total duration of 1400 hours. Excess heat was first observed after 443 hours of electrolysis and was observed in bursts on four separate occasions. The maximum excess power observed was 2.0 watts (W) (53% in excess of the input power); the total excess of energy was 1.07 MJ or 30 MJ/mole of Pd.

### Example 3

#### Cell 67

FIG. 6 shows a cell 67 which operates at approximately atmospheric pressure. The vessel 69 is constructed of Al and has a cylindrical sleeve shape with an internal surface of PTFE. Positioned along the central axis of vessel 69 is palladium cathode 55. A cathode current connection 83 and an anode connection 85 are attached.

The electrolysis portion of the cell 67 is exposed only to the materials palladium, platinum, quartz glass, and PTFE. Anode 65 consists of an approximately 1.0m long piece of 0.5mm dia. Pt wire wound around a cage 73 of five quartz glass rods held in place by two PTFE discs 75. The wire 65 is held in place by attachment to 2mm Pd mounting posts 79 mounted on the top PTFE disk 75. Separating the cathode 55 and anode 65 is electrolyte 71 consisting of LiOD in D<sub>2</sub>O. Reference electrode 63 is positioned adjacent to cathode 55. All cell 67 surfaces are solvent cleaned and rinsed. The anode cage 73 is further washed with aqua regia and rinsed with D<sub>2</sub>O.

#### Cathode 55

The Pd cathode 55 is a 3mm dia. 3 cm long Pd rod, machined from a 1/8" pure Pd wire. Prior to insertion into vessel 69, cathode 55 is solvent cleaned, vacuum annealed at 800°C for two to three hours, and slowly cooled in an atmosphere of Ar. Cathode 55 is finally dipped in heavy aqua regia for 20 seconds and rinsed with D<sub>2</sub>O.

#### Electrolyte 71 Preparation

The LiOD electrolyte 71, with 200 ppm (molar) Al, is manufactured by adding 0.175g Li metal and approximately 7 mg pure Al foil to 25 ml D<sub>2</sub>O. This procedure is carried out under a nitrogen atmosphere. Electrolyte 71 should be prepared immediately prior to use.

#### Cell 67 Assembly

An external 180 ohm heater (0.04" dia 72" long) is wound around the outside of vessel 69 within specially machined grooves on the surface 59. These grooves are omitted from the drawing of FIG. 6. Cell 67 is assembled with minimum exposure to air or H<sub>2</sub>O.

Approximately 20 ml of 1M LiOD with ~ 200 ppm (molar) Al is added to vessel 69. A 1/8" outside diameter Ni tube 81, extending out of cell 67, is attached on the top of vessel 69. Vessel 69 is pressurized to 50 psig with D<sub>2</sub>.

- 5 Using this procedure and apparatus, a calorimetry experiment was performed with a total duration of 1630 hours. Excess heat was first observed after 308 hours of electrolysis and was observed on ten separate occasions, in all cases initiated during and persisted after the conclusion of an
- 10 increasing current ramp. The maximum excess power observed was 1.0 watts (W) (10% in excess of the input power); the total excess of energy was 1.08 MJ or 45 MJ/mole of Pd.

The invention has now been explained with reference to specific embodiments which involve the charging of palladium

15 with deuterium. Other embodiments, which can involve the charging of other metal cathodes with other hydrogen isotopes, will be apparent to those of ordinary skill in the art in light of this disclosure. Therefore, it is not intended that this invention be limited, except as indicated

20 by the appended claims.

WHAT IS CLAIMED IS:

1. A method for forming a film on a metal cathode, said method comprising the steps of:
  - immersing the metal cathode in an electrolyte  
5 containing an isotope of hydrogen and other elemental species; and
  - holding the cathode at a negative potential to generate in the cathode an electrical current to allow said other elemental species to form a film on said cathode;  
10 said current further facilitating the loading of the hydrogen isotope from the electrolyte into the cathode.
2. A method for forming a film on a palladium cathode, said method comprising the steps of:
  - immersing the palladium cathode in an electrolyte  
15 containing D<sub>2</sub>O and other elemental species;
  - holding the cathode at a negative potential to generate in the cathode an electrical current to allow said other elemental species to form a film on said cathode; and
  - said current further facilitating the loading of  
20 deuterium from the electrolyte into the cathode.
3. The method of claim 1, wherein said species are selected from the group of elements comprising Al, Si, B, Ti, Li, Sc, Zr, Y, Mg, Ca, Ba, Fe, Ni, Cu, and V.
4. The method of claim 1, wherein the step of holding the  
25 cathode at a negative potential induces the movement of said other elemental species to said cathode.
5. The method of claim 2, further comprising the step of:
  - supplying energy to the loaded deuterium to allow deuterium to interact and generate heat.
- 30 6. The method of claim 5, wherein the step of supplying energy to the loaded deuterium is fostered by applying an electrical current to the cathode.

7. The method of claim 1, further comprising an initial step of depositing Pd onto a metallic rod to form the cathode.

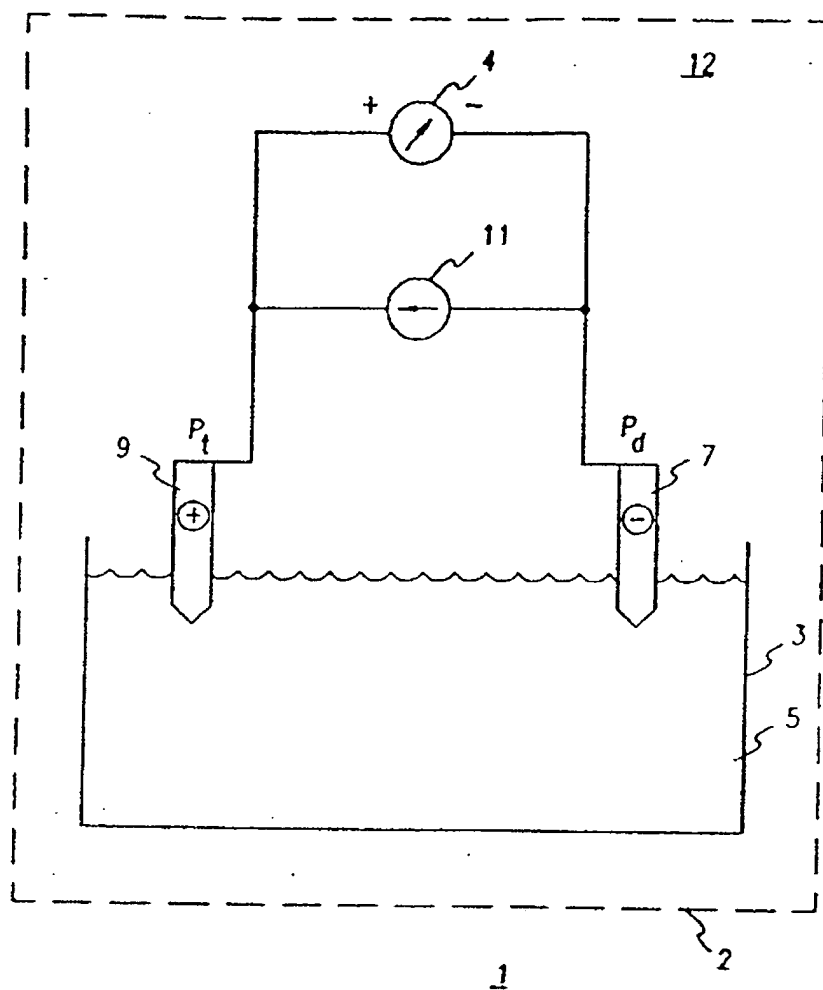


FIG. 1



2/6

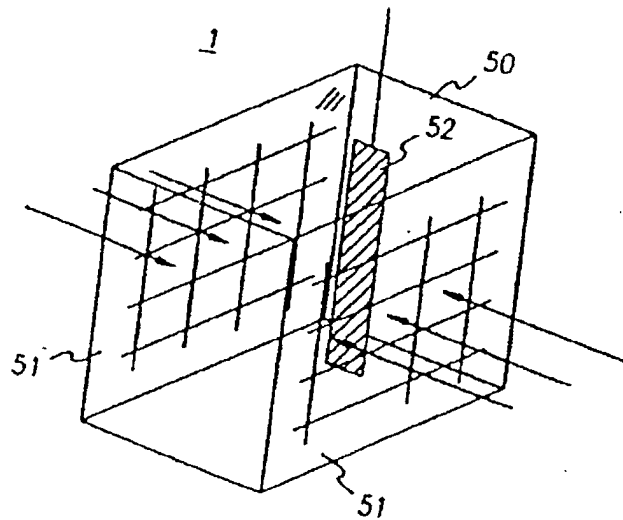


FIG. 2

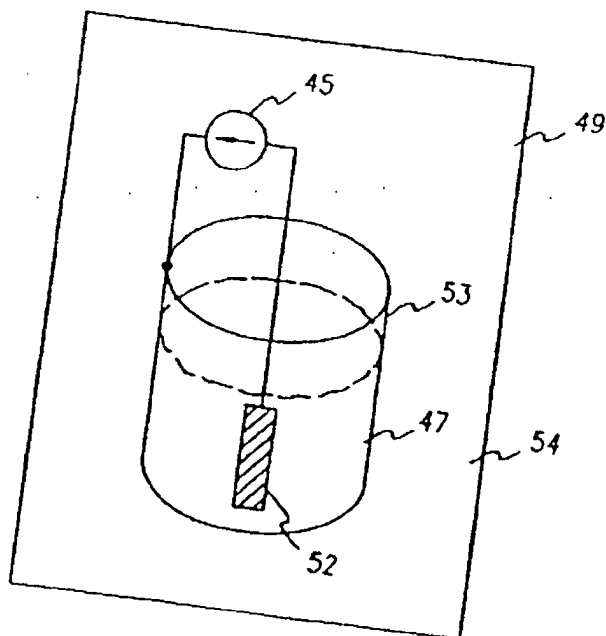


FIG. 3

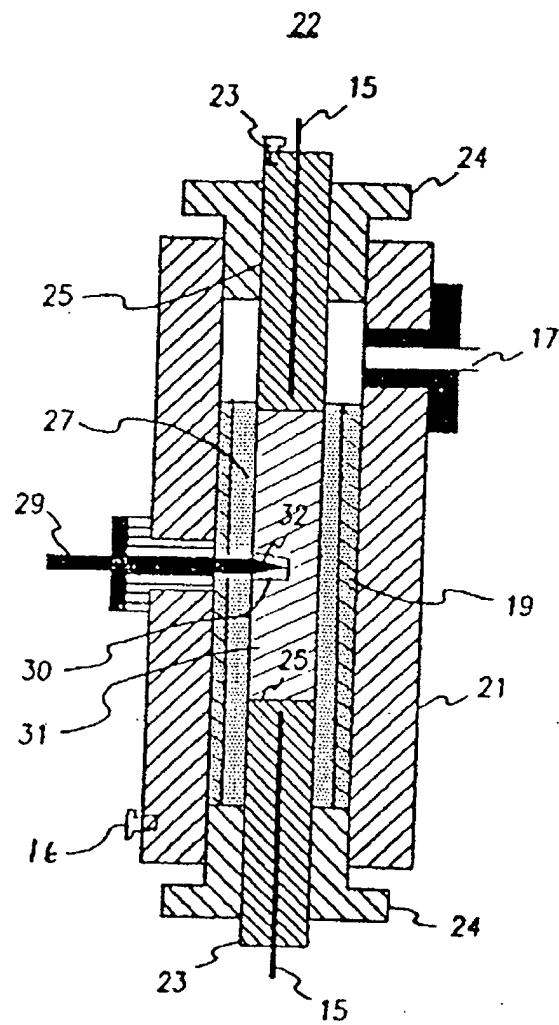


FIG. 4

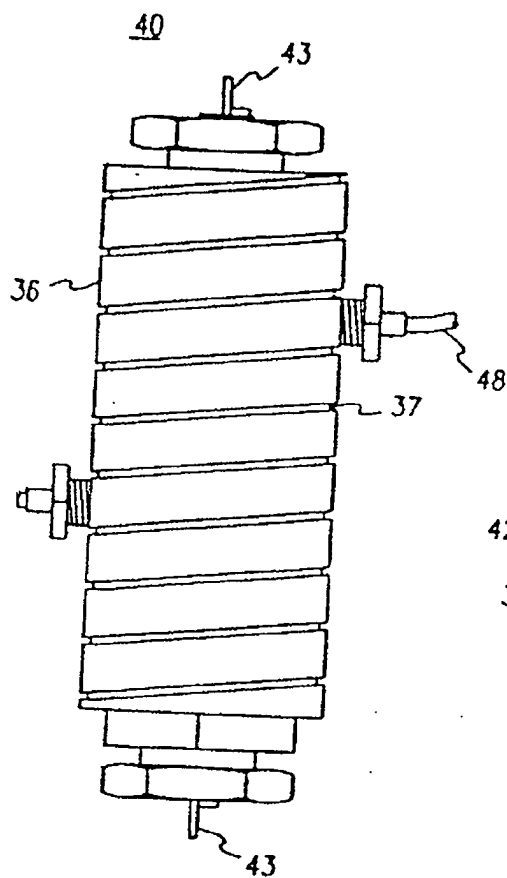


FIG. 5a

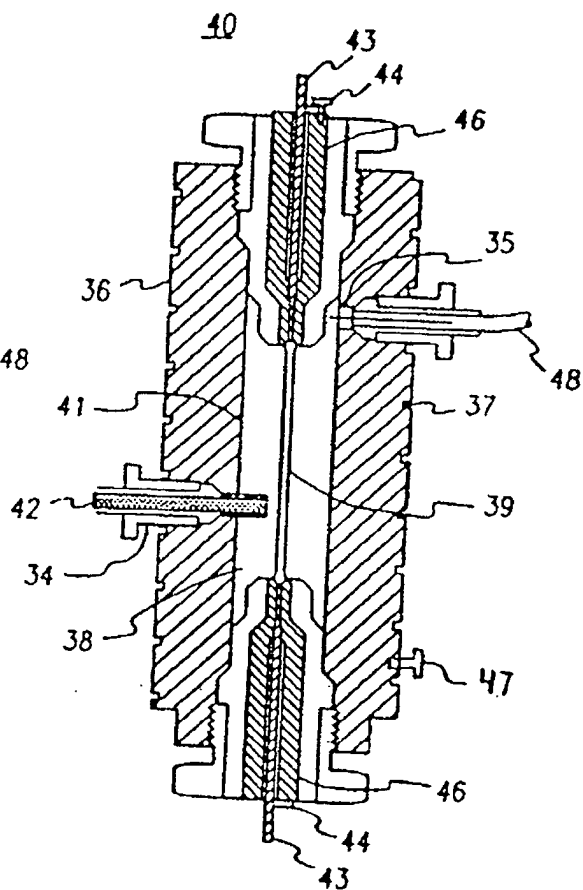


FIG. 5b

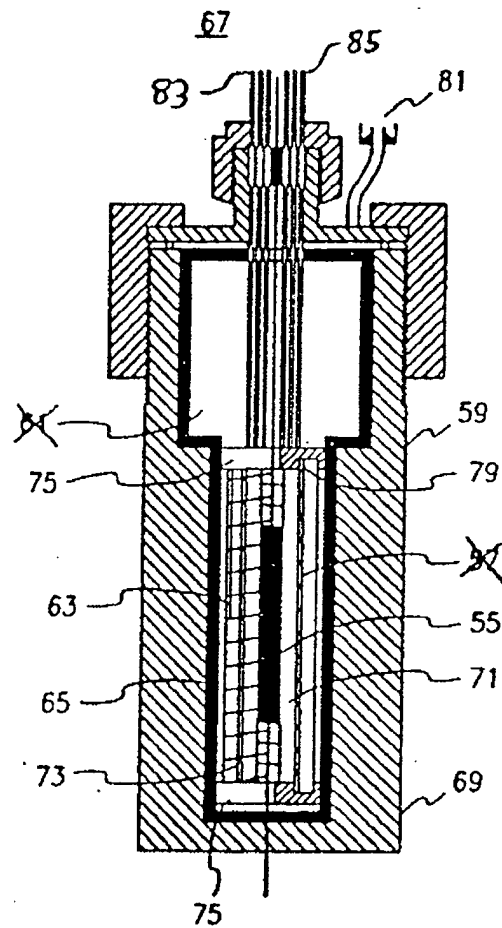


FIG. 6

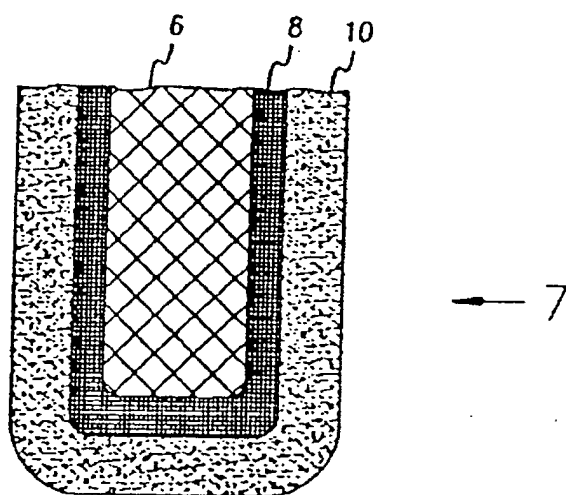


FIG. 7

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/11754

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(S) : G21B 1/00  
US CL : 376/100

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
U.S. : 376/100,146; 204/129, 290R, 290F; 205/316,333

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO, A, 90/10935 (PONS ET AL.) 20 September 1990, Note pages 19, 31, 32, 34.	1-7
X	US, A, 4,986,887 (GUPTA ET AL.) 22 January 1991.	1-6
X	US, A, 4,487,670 (BELLANGER ET AL.) 11 December 1984, see cols 3 and 4.	1-7
X	US, A, 1,442,238 (SMITH) 16 January 1923.	1-6
X	US, A, 2,534,234 (COX) 19 December 1950.	1-6
<u>Y</u> <u>X</u> <u>L</u>	JOURNAL OF FUSION ENERGY, Vol. 9, No. 2, (June 1990), pages 133-148, Albagli et al, (also cited as casting doubt on inducing cold fusion by forcing deuterium into palladium).	<u>7</u> <u>1-6</u> <u>1-7</u>

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A document defining the general state of the art which is not considered to be part of particular relevance	* X document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
* E earlier document published on or after the international filing date	* Y document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
* I document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	* & document member of the same patent family
* U document referring to an oral disclosure, use, exhibition or other means	
* P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  
02 MARCH 1994

Date of mailing of the international search report  
25 MAR 1994

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Authorized officer  
HARVEY E. BEHREND

Facsimile No. (703) 305-3230

Telephone No. (703) 308-0439

Form PCT/ISA/210 (second sheet) (July 1992)\*

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/11754

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
<u>Y</u> <u>L</u>	PHYSICIA SCRIPTA, Vol. 40, (September 1989), pages 303-306, Sundqvist et al, (also cited as casting doubt on inducing cold fusion by forcing deuterium into palladium).	<u>7</u> <u>1-7</u>
<u>Y</u> <u>X</u> <u>L</u>	NATURE, Vol. 342, 23 November 1989, pages 375-384, Williams et al, (note page 380), (also cited as casting doubt on inducing cold fusion by forcing deuterium into palladium).	<u>7</u> <u>1-6</u> <u>1-7</u>
<u>Y</u> <u>X</u> <u>L</u>	PHYSICAL REVIEW LETTERS, Vol. 62, No. 25, 19 June 1989, pages 2929-2932 (note the second column on page 2930) Ziegler et al, (also cited as casting doubt on inducing cold fusion by forcing deuterium into palladium)	<u>7</u> <u>1-6</u> <u>1-7</u>